Uncovering the charge transfer and recombination mechanism in ZnS-coated PbS quantum dot sensitized solar cells

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ABSTRACT

In this work, the charge transfer and recombination mechanism is uncovered for the PbS/ZnS quantum dot sensitized solar cells (QDSSCs) based on nanoporous TiO₂ electrodes. PbS quantum dots (QDs) were in-situ grown on TiO₂ nanoparticles through the successive ionic absorption and reaction (SILAR) method, followed by the surface passivation of ZnS for the sensitized electrodes. It was observed that the ZnS coating cycles play a significant role in determining the photovoltaic parameters. The highest power conversion efficiency of 1.4% was achieved by coating 13 cycles of ZnS on TiO₂/PbS electrode. It is essential to understand why and how ZnS passivation layers improve the photovoltaic performance of PbS QDSSCs. All obtained solar cells were characterized thoroughly by optical and electrical techniques. The open-circuit voltage decay technique and electrochemical impedance measurements indicated that the ZnS passivation layers significantly suppressed the charge recombination at the

TiO₂/electrolyte and TiO₂/QD interfaces. The transient grating measurements suggested that the electron injection from PbS QDs to TiO₂ was obviously enhanced by the ZnS coating layers. This could be attributed to the reduction of carrier trapping and recombination in PbS QDs after surface passivation. These beneficial effects of ZnS layers, therefore, resulted in the improved photovoltaic performances of PbS QDSSCs. This work provides better understanding on the passivation effect of ZnS layers in PbS QDSSCs, which would be beneficial for the further improvement of QDSSCs.

Keywords: Quantum dot sensitized solar cells; Charge transfer; Recombination; Transient grating

I. INTRODUCTION

Narrow-band-gap semiconductor quantum dots (QDs), such as CdS, CdSe, PbS, and CuInS₂ QDs are attracting growing attention as promising sensitizer candidates for solar cells (Chen, et al., 2010; Diguna, et al., 2007; Gonzalez-Pedro, et al., 2013; Konovalov, et al., 2015; Pan, et al., 2014; Santra, et al., 2013; Shen, et al., 2010b; Zhang, et al., 2012). In comparison with traditional dye sensitizers, QDs possess unique advantages such as high extinction coefficient, tunable band-gap structures, large intrinsic dipole, and the possibility of multiple exciton generation (MEG) (Shen, et al., 2008b). The MEG effect can lead to over 100% quantum yield and enhance the performances of photovoltaic devices, which has been evidenced in previous literatures (Lin, et al., 2011; Luque, et al., 2007; Sambur, et al., 2010). It was predicted that the power conversion efficiency (PCE) of photovoltaic devices could be increased up to 44% by tuning the band gap of QDs and generating multiple electron-hole pairs with one single photon absorption (Hanna and Nozik, 2006). However, the PCE of quantum dot sensitized solar cells (QDSSCs) is lagging behind that of dye-sensitized solar cells (DSSCs) (Emin, et al., 2011; Yum, et al., 2014). This is mainly attributed to the large amount of defects on QD surfaces, which serve as the trapping states for photoexcited carriers and thus lead to the poor photovoltaic performances (Prezhdo, 2009). To solve this problem, the surface of QD-sensitized electrodes are often modified by coating a wide band gap semiconducting material or exchanging the native long capping ligands with short ones.

Our previous studies have demonstrated that coating ZnS layers over QD-sensitized electrodes was a powerful approach to improve the device stability and photovoltaic properties of quantum dot sensitized solar cells (Diguna; Shen; Kobayashi and Toyoda, 2007; Guijarro, et al., 2011; Shen; Kobayashi; Diguna and Toyoda, 2008b; Sixto, et al., 2009). Although extensive effort has been devoted to investigate the role of passivation layers, the detailed mechanism is still not fully understood. In this work, therefore, the effects of passivation layers on the photovoltaic properties and charge transfer/recombination mechanism are investigated for PbS quantum dot sensitized solar cells. PbS QDSSCs with different ZnS passivation cycles were thoroughly characterized using the open circuit voltage decay (OCVD), electrochemical impedance spectroscopy (EIS), and an improved transient grating (TG) technique. It was revealed that the enhanced photovoltaic performances in PbS/ZnS QDSSCs were mainly attributed to the passivation effect of ZnS layers on TiO₂ photoanodes and PbS QD surface states, which prevented the electron trapping on QD surfaces, the electron back transfer from electrodes to electrolyte, and the interfacial recombination at TiO₂/PbS interfaces.

II. EXPERIMENTAL DETAILS

Nanoporous TiO₂ electrodes were prepared on pre-cleaned FTO glasses by a doctor blading method as reported in previous literature (Shen, et al., 2005; Shen and Toyoda, 2003). Anatase TiO₂ nanoparticles (DSL 18-NRT, 20 nm average diameter) were mixed with distilled water (30 wt.%), acetylacetone (10 wt.%) and polyethylene glycol (PEG, 40 wt.% relative to TiO₂) to form a white paste. The obtained pastes were deposited on fluorine-doped-tin-oxide (FTO) coated glasses (Pilkington, ~15 $\Omega/\square$ resistance) using a Scotch tape as the spacer. PbS/ZnS QDs layers were deposited on TiO₂ electrodes using the successive ionic-layer adsorption and reaction (SILAR) method, which involves the layer-by-layer growth of QDs by sequentially immersing substrates into ionic precursor solutions for 30 s. Here, a 0.05 M lead nitrate aqueous solution was used as the lead source for the deposition of PbS QDs, and a 0.1 M zinc acetate aqueous solution was used as the zinc source for the coating of ZnS

passivation layers. The sulfide sources were 0.05 M and 0.1 M sodium sulfide aqueous solutions for deposition of PbS and ZnS, respectively. After each dipping step in a precursor solution, the electrodes were rinsed with distilled water to remove the excess of precursors. Two SILAR cycles were applied for the deposition of PbS QDs, while different cycles (4, 8, 13, 20) were carried out for the coating of ZnS layers. Quantum dot sensitized solar cells were fabricated by sandwiching the sensitized-TiO₂ electrodes with Cu₂S counter electrodes using a polysulfide aqueous solution as the redox electrolyte. The electrolyte was an aqueous solution containing 1 M Na₂S and 1 M S. The Cu₂S counter electrodes were prepared by immersing brass in 30% HCl at 70 °C for 5 min and subsequently dipping them into the polysulfide solution for 10 min.(Toyoda, et al., 2010) For the TG measurements, PbS-sensitized TiO₂ electrodes were prepared by coating 0, 5, and 13 cycles of ZnS on TiO₂/PbS electrodes. The morphology and composition of electrodes were investigated by a high-resolution transmission electron microscopy (HR-TEM, JEM-2100F) equipped with an energy dispersive X-ray (EDX) spectroscope.

The current density-voltage (*J-V*) measurements were performed under dark and AM 1.5G irradiation (100 mW/cm²), respectively, using a Keithley 2400 source meter with a Peccell solar simulator PEC-L10. The active area of fabricated solar cells was 0.24 cm². The incident photon conversion efficiency (IPCE) spectra were measured under illumination using a Nikon G250 monochromator equipped with a 300 W Xe arc lamp. The open-circuit voltage decay (OCVD) measurements were carried out using a 405 nm diode laser and the voltage responses were recorded using an Iwatsu digital oscilloscope DS-5554. The OCVD measurements were performed without a background light bias. Electrochemical impedance spectroscopy measurements were performed under dark conditions using an impedance analyzer (BioLogic, SP-300) by applying a small voltage perturbation (10 mV rms) at frequencies from 1 MHz to 0.1 Hz for different forward bias voltages. The improved transient grating measurements were performed using a titanium/sapphire laser (CPA-2010, Clark-MXP Inc.) with a wavelength of 775 nm, a repetition rate of 1 kHz, and a pulse width of 150 fs.

The light was separated into two beams. One beam was used as the probe pulse; the other one as the pump light to pump an optical parametric amplifier (TOAPS from Quantronix) and generate light pulses with wavelength tunable from 290 nm to 3 μm . In this work, the pump pulse wavelength was 520 nm and the probe pulse wavelength was 775 nm. Typical laser pulse intensity used in the TG measurement was 2.0 mW or less than it. The area of the laser beam was around 0.2 cm^2 . All the TG measurements are carried out in N_2 atmosphere. All tested samples showed negligible photo-damage during the TG measurements. The detailed principle of the improved TG technique can be found in our previous literature (Gonzalez-Pedro; Sima; Marzari; Boix; Gimenez; Shen; Dittrich and Mora-Sero, 2013; Guijarro; Campina; Shen; Toyoda; Lana-Villarreal and Gomez, 2011; Shen, et al., 2010a; Shen, et al., 2008a; Shen; Katayama; Yamaguchi; Sawada and Toyoda, 2005; Yang, et al., 2014).

III. RESULTS AND DISCUSSION

To confirm the formation of PbS/ZnS layers on TiO_2 electrodes, the morphology and elemental composition of obtained samples were investigated by HR-TEM and EDX measurements. Fig. 1a shows the bright field scanning transmission electron microscopy (STEM) image of the PbS-sensitized TiO_2 electrode coated with 13 SILAR cycles of ZnS. The lattice spacing (0.33 nm) as labelled in Fig. 1a was assigned to the distance between (101) planes in anatase TiO_2 crystals. The corresponding annular dark field (ADF) STEM image is shown in Fig. 1b. Due to the atomic-number (Z) sensitive nature of the ADF contrast, the dark and bright areas could be assigned to TiO_2 and PbS/ZnS, respectively. The thickness of PbS/ZnS layer was determined to be around 4 nm. Fig. 1c and 1d present a STEM image and the corresponding EDX mapping images of the obtained electrode, respectively. It was shown that lead, zinc, and sulfur elements were evenly distributed over the electrode, which verified that uniform QD layers were successfully formed on TiO_2 surfaces by the SILAR method.

FIG. 1 (a, b) Bright field and dark field STEM images of TiO_2/PbS electrode coated with 13 cycles of ZnS, respectively. (c, d) STEM image and the EDX mapping of ZnS-coated TiO_2/PbS electrode, respectively. The scale bars represent 2 nm in (a, b), and 10 nm in (c, d).

FIG. 2 Schematic diagram of the PbS/ZnS sensitized solar cells. The solid arrows indicate the excitation of PbS QDs and the injection/transfer of photoexcited charges. The dotted arrows indicate the charge recombination at the $\text{TiO}_2/\text{QD}/\text{electrolyte}$ interfaces.

After the characterization of sensitized TiO_2 electrodes, QDSSCs with the sandwich structure were fabricated by a typical method. The detailed structure and working principle of the photovoltaic devices is shown in Fig. 2. The devices are composed of the QD-sensitized electrode, the polysulfide electrolyte

and a Cu₂S counter electrode on brass. It was observed the photovoltaic performance of PbS QDSSCs was very poor (see the *J-V* curve in Fig. S1) without the ZnS coating for TiO₂/PbS anode, and the cell was unstable for a repeated measurement. By contrast, the cell stability was significantly enhanced by coating ZnS layers on TiO₂/PbS. As shown in Fig. S2, the photovoltaic properties of one of the PbS(2)/ZnS(5) solar cell were relatively stable in 60 min under irradiation. The thickness of PbS QDs were optimized by fixing the ZnS layer as 13 SILAR cycles. As shown in Fig. S3, the cell with 2 SILAR cycles of PbS gave the highest short circuit current (J_{sc}) and the best efficiency. Then, the effect of ZnS thickness on QDSSCs was investigated by using 2 cycles of PbS and different cycles of ZnS. The *J-V* curves and the corresponding photovoltaic parameters are shown in Fig. 3a and Table 1, respectively. As can be seen that the value of short circuit current (J_{sc}) was significantly improved from 3.3 mA/cm² to 8.4 mA/cm² as the ZnS coating was increased from 4 to 13 cycles. As the ZnS deposition were increased to 20 cycles, the J_{sc} value show a slight decrease. On the other hand, the value of open circuit voltage (V_{oc}) was improved steadily and saturated approximately at 0.37 V as the increase of ZnS cycles. The highest efficiency was achieved as 1.4% by coating 13 cycles ZnS on TiO₂/PbS electrodes. Fig. 3b shows the incident photon-to-current conversion efficiency (IPCE) spectra of fabricated QDSSCs, with the calculated photocurrent consistent with the measured J_{sc} values. Corresponding to the photocurrent density, the highest IPCE value was also obtained for the device with 13 cycles ZnS. The improved photovoltaic performance in ZnS-coated PbS QDSSCs could be attributed to the decrease in PbS surface states. In the case of 20 cycles ZnS, significant amount of ZnS QDs were deposited on PbS surfaces, which is deleterious for the effective hole transfer to the electrolyte. Consequently, the recombination of electrons and holes within PbS QDs was increased, which resulted in the decrease of J_{sc} and IPCE values.

FIG. 3 J - V curves (a) and IPCE spectra (b) of PbS QDSSCs with various ZnS coating cycles (4, 8, 13, 20 cycles) on TiO₂/PbS electrodes.

TABLE 1. Photovoltaic parameters of PbS QD-sensitized solar cells with different ZnS-coating cycles.

ZnS cycles	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
4	3.3 ± 0.02	0.25 ± 0.002	0.44 ± 0.002	0.37 ± 0.003
8	5.5 ± 0.03	0.30 ± 0.006	0.50 ± 0.008	0.83 ± 0.01
13	8.4 ± 0.01	0.36 ± 0.003	0.45 ± 0.004	1.40 ± 0.007
20	3.7 ± 0.02	0.37 ± 0.002	0.43 ± 0.003	0.61 ± 0.008

FIG. 4 Open-circuit voltage decay curves (a) and the calculated electron lifetime (b) of PbS QDSSCs with various ZnS-coating cycles.

It is well known that the charge-transfer and recombination dynamics play significant roles in determining the photovoltaic performances of solar cells (Mora-Seró, et al., 2009). To clarify the effects of ZnS layers on the recombination process in PbS QDSSCs, open circuit voltage decay measurements were carried out for above solar cells. Fig. 4a shows the OCVD curves of PbS QDSSCs with various ZnS cycles after a 405 nm laser pulse excitation. It is shown that the V_{oc} decay in PbS QDSSCs was significantly slowed by increasing the ZnS coating cycles. This could be attributed to the reduction of charge recombination at the electrode/electrolyte interfaces. In the other word, the ZnS buffer layers hindered the electron back transfer from the TiO_2 electrode to the polysulfide electrolyte, and also reduced the charge recombination between TiO_2 electrodes and PbS QDs. From the OCVD measurement results, the effective lifetime (τ_n) of electrons in TiO_2 was calculated from the voltage decay curves according to the equation (1) (Zaban, et al., 2003):

$$\tau_n = - \frac{k_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad (1)$$

where $k_B T$ is the thermal energy; e is the positive elementary charge. As shown in Fig. 4b, the electron lifetime was significantly increased as increasing the ZnS coating cycles. These results suggested that

the sources of recombination for the lower V_{oc} in PbS QDSSCs are: i) the charge recombination between TiO_2 and PbS QDs due to the interfacial defects and/or the surface defects in PbS QDs; ii) the electron back transfer from TiO_2 electrodes to the polysulfide electrolyte directly through QDs and interface/surface states. The ZnS cycle-dependent change of voltage decay and electron lifetime indicated that ZnS coating effectively suppressed the recombination in PbS QDSSCs.

FIG. 5 (a) Impedance spectra of ZnS-coated PbS QDSSCs measured at a forward bias of 0.35 V under dark conditions. (b) Chemical capacitance (C_μ) and (c) recombination resistance (R_{rec}) as a function of applied voltage V_F for PbS QDSSCs with different ZnS coating cycles.

To further investigate the effect of ZnS coating on the performances of PbS QDSSCs, fabricated cells were characterized by the EIS technique and analyzed with the standard models for QDSSCs (González-Pedro, et al., 2010). Fig. 5a shows the impedance spectra of PbS QDSSCs measured at a forward bias of 0.35 V under dark conditions. Two semicircles were observed from the impedance spectra: the small semicircle at the high frequency is associated with the charge transfer at the counter electrode/electrolyte interface; and the large semicircle at the low frequency is associated with the charge transfer at the TiO_2 /PbS/electrolyte interfaces (Lai, et al., 2014). It is shown that the charge transfer resistance at the TiO_2 /PbS/electrolyte interface was significantly increased after ZnS coating, indicating photo-generated electrons in the modified electrodes were more difficult to recombine. The calculated chemical capacitance (C_μ) and recombination resistance (R_{rec}) were plotted against a corrected voltage scale, which was the voltage drop (V_F) in the sensitized electrode, obtained by

subtracting the voltage drop in series resistance from the applied bias. The analysis of C_μ indicated that the TiO_2 conduction band (CB) was downward shifted with the increase of ZnS cycles (Fig. 5b). The increasing amount of ZnS prevented the direct contact of electrolyte ($\text{pH} \approx 12$) with TiO_2 , thus decreased the effective pH of TiO_2 surface and reduced its CB position (Rothenberger, et al., 1992). In addition, PbS QDSSCs exhibited higher value of R_{rec} (lower recombination rate) as the increase of ZnS cycles (Fig. 5c). Considering the increase in V_{oc} as the increase of ZnS layers, the impedance results suggested that the recombination at $\text{TiO}_2/\text{electrolyte}$ interface was effectively reduced by the ZnS layers, which was consistent with the results obtained from OCVD measurements.

FIG. 6 (a) TG responses of TiO_2/PbS electrodes with and without ZnS coating. (b) The comparison between proportionality constants calculated from TG responses and IPCE values (at 520 nm wavelength) of PbS QDSSCs with different ZnS cycles.

In addition to the recombination process, electron transfer kinetics also play an important role in determining the photovoltaic performances of QDSSCs. An improved transient grating technique has proved to be a useful method to investigate the relaxation of carriers or excited species in various materials (Katayama, et al., 2003; Yang; Oshima; Yindeesuk; Pan; Zhong and Shen, 2014). Fig. 6a shows the comparison of transient grating responses along with fitted curves of PbS-sensitized TiO_2 electrodes with different ZnS cycles. According to the working principle of TG technique, the intensity

of TG response is proportional to the refractive index change ($\Delta n(t)$) of samples due to the photoexcitation process. The refractive index change can be approximately calculated by the following equation (Gonzalez-Pedro; Sima; Marzari; Boix; Gimenez; Shen; Dittrich and Mora-Sero, 2013; Shen, et al., 2006; Shen; Katayama; Yamaguchi; Sawada and Toyoda, 2005):

$$\Delta n(t) = A \left(\frac{N_e(t)}{m_e} + \frac{N_h(t)}{m_h} \right) \quad (2)$$

where A is proportionality constant; $N_e(t)$ and $N_h(t)$ are the photoexcited electron and hole densities, respectively; m_e and m_h are the effective masses of electrons and holes, respectively. According to eq. (2), the contribution of electrons and holes to $\Delta n(t)$ is inversely proportional to their effective masses. It is known that the effective electron mass of TiO_2 is approximate $30 m_0$ (m_0 is the electron rest mass), which is two orders larger than that of PbS ($0.09 m_0$) (Preier, 1979). Therefore, the effect of injected electrons in TiO_2 was negligible for the TG signal intensity.

TABLE 2. Fitting parameters obtained from the TG responses of TiO_2/PbS electrodes with and without ZnS coating.

ZnS Cycles	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3
0	0.37	9.9 ± 1.1	0.38	127 ± 20	0.24
5	0.28	9.5 ± 1.0	0.30	148 ± 23	0.42
13	0.22	3.4 ± 0.4	0.20	76 ± 10	0.58

It was observed the TG signal of PbS -sensitized electrodes consisted of three decay processes and could be well fitted with a double exponential decay plus an offset, as shown in the following equation:

$$y(t) = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} + A_3 \quad (3)$$

where A_1 , A_2 , and A_3 are proportionality constants; τ_1 and τ_2 are time constants of the corresponding decay processes. The fitting parameters including the time constants and proportionality constants are listed in Table 2. For the electrode without ZnS coating, the first and second decay processes occur within the initial several to tens of picoseconds, followed by a slow decay after hundreds of picoseconds. In this work, the overall TG signal decay reflects the decrease of photoexcited electron/hole densities in PbS QDs. It was reported that electron injection from PbS QDs to TiO₂ electrodes occurred in the timescale of 100 ns and the radiative lifetime of photoexcited carriers in PbS QDs was in the timescale of microseconds (Hyun, et al., 2008; Jamie, et al., 2005). Based on these results, and considering the large amount of defects on PbS surfaces, it is reasonable to propose that the first two decay processes can be assigned to the electron and hole trapping, while the third decay process corresponds to the electron injection from PbS QDs to TiO₂ electrodes.

As shown in Fig. 6a, ZnS-coated electrodes show slower TG decay curves compared with that of the bare TiO₂/PbS electrode. After ZnS coating, the time constants of the two fast decay processes tended to decrease (with exception of τ_2 in the sample with 5 cycle ZnS), which could be related with the change of PbS surface states. More importantly, the proportionality constants A_1 and A_2 decreased, while A_3 increased with the ZnS cycles increasing (Fig.5b). This result suggested that ZnS layers reduced the proportion of charge trapping in PbS QDs and simultaneously enhanced the electron injection from PbS QDs to TiO₂ electrodes. Additional proof of this conclusion was obtained by comparing the tendency of proportionality constants and that of IPCE values as shown in Fig. 6(b). It was shown that the ZnS-cycle dependent change of A_3 was exactly same with that of the IPCE values obtained at 520 nm wavelength, which was the excitation wavelength for TG measurements. This verified our suggestion that ZnS coating enhanced the electron injection efficiency at the TiO₂/PbS interface by reducing surface states of the PbS QDs. It should be noted that the IPCE value of the PbS QDSSCs is still as low as 50% even after coating the ZnS layers. We proposed that this could be due to the lattice parameter mismatch

between PbS ($a = 5.936 \text{ \AA}$) and ZnS ($a = 5.41 \text{ \AA}$) crystals, leading to imperfect surface passivation of PbS QDs by ZnS coating. The investigation on various lattice-matched materials is underway to further improve the surface passivation of PbS QDSSCs and therefore enhance the photovoltaic performances including the IPCE values.

IV. CONCLUSION

In conclusion, the photovoltaic performances of PbS QDSSCs were significantly improved by coating ZnS over TiO_2/PbS electrodes. The improvement was mainly attributed to the enhanced electron injection efficiency from PbS to TiO_2 , and the suppressed charge recombination at the $\text{TiO}_2/\text{PbS}/\text{electrolyte}$ interface. This mechanism was first-time revealed for ZnS-coated PbS QDSSCs by the open circuit voltage decay measurement, impedance spectroscopy, and the transient grating technique. Our findings clearly demonstrate that surface passivation on QDs can improve photovoltaic performances of QDSSCs by enhancing the charge separation and suppressing the charge recombination. It has demonstrated that appropriate surface passivation on QDs is an important stringency for improving the photovoltaic performances of QDSSCs.

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REFERENCES

Chen, H., Li, W., Liu, H., Zhu, L., 2010. A suitable deposition method of CdS for high performance CdS-sensitized ZnO electrodes: Sequential chemical bath deposition. *Sol. Energy*, 84, 1201-1207.

Diguna, L.J., Shen, Q., Kobayashi, J., Toyoda, T., 2007. High efficiency of CdSe quantum-dot-sensitized TiO_2 inverse opal solar cells. *Appl. Phys. Lett.*, 91, 023116.

Emin, S., Singh, S.P., Han, L., Satoh, N., Islam, A., 2011. Colloidal quantum dot solar cells. *Sol. Energy*, 85, 1264-1282.

González-Pedro, V., Xu, X., Mora-Seró, I., Bisquert, J., 2010. Modeling High-Efficiency Quantum Dot Sensitized Solar Cells. *ACS Nano*, 4, 5783-5790.

Gonzalez-Pedro, V., Sima, C., Marzari, G., Boix, P.P., Gimenez, S., Shen, Q., Dittrich, T., Mora-Sero, I., 2013. High performance PbS Quantum Dot Sensitized Solar Cells exceeding 4% efficiency: the role of metal precursors in the electron injection and charge separation. *Phys. Chem. Chem. Phys.*, 15, 13835-13843.

Guijarro, N., Campina, J.M., Shen, Q., Toyoda, T., Lana-Villarreal, T., Gomez, R., 2011. Uncovering the role of the ZnS treatment in the performance of quantum dot sensitized solar cells. *Phys. Chem. Chem. Phys.*, 13, 12024-12032.

Hanna, M.C., Nozik, A.J., 2006. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *Journal of Applied Physics*, 100, 074510.

Hyun, B.-R., Zhong, Y.-W., Bartnik, A.C., Sun, L., Abruña, H.D., Wise, F.W., Goodreau, J.D., Matthews, J.R., Leslie, T.M., Borrelli, N.F., 2008. Electron Injection from Colloidal PbS Quantum Dots into Titanium Dioxide Nanoparticles. *ACS Nano*, 2, 2206-2212.

Jamie, H.W., Elizabeth, T., Andrew, R.W., Norman, R.H., Halina, R.-D., 2005. Time-resolved photoluminescence spectroscopy of ligand-capped PbS nanocrystals. *Nanotechnology*, 16, 175.

Katayama, K., Yamaguchi, M., Sawada, T., 2003. Lens-free heterodyne detection for transient grating experiments. *Appl. Phys. Lett.*, 82, 2775-2777.

Konovalov, I., Emelianov, V., Linke, R., 2015. Hot carrier solar cell with semi infinite energy filtering. *Sol. Energy*, 111, 1-9.

Lai, L.-H., Protesescu, L., Kovalenko, M.V., Loi, M.A., 2014. Sensitized solar cells with colloidal PbS-CdS core-shell quantum dots. *Phys. Chem. Chem. Phys.*, 16, 736-742.

Lin, Z., Franceschetti, A., Lusk, M.T., 2011. Size Dependence of the Multiple Exciton Generation Rate in CdSe Quantum Dots. *ACS Nano*, 5, 2503-2511.

Luque, A., Martí, A., Nozik, A.J., 2007. Solar Cells Based on Quantum Dots: Multiple Exciton Generation and Intermediate Bands. *MRS Bull.*, 32, 236-241.

Mora-Seró, I., Giménez, S., Fabregat-Santiago, F., Gómez, R., Shen, Q., Toyoda, T., Bisquert, J., 2009. Recombination in Quantum Dot Sensitized Solar Cells. *Acc. Chem. Res.*, 42, 1848-1857.

Pan, Z., Mora-Seró, I., Shen, Q., Zhang, H., Li, Y., Zhao, K., Wang, J., Zhong, X., Bisquert, J., 2014. High-Efficiency “Green” Quantum Dot Solar Cells. *J. Am. Chem. Soc.*, 136, 9203-9210.

Preier, H., 1979. Recent advances in lead-chalcogenide diode lasers. *Appl. Phys.*, 20, 189-206.

Prezhdo, O.V., 2009. Photoinduced Dynamics in Semiconductor Quantum Dots: Insights from Time-Domain ab Initio Studies. *Acc. Chem. Res.*, 42, 2005-2016.

Rothenberger, G., Fitzmaurice, D., Graetzel, M., 1992. Spectroscopy of conduction band electrons in transparent metal oxide semiconductor films: optical determination of the flatband potential of colloidal titanium dioxide films. *J. Phys. Chem.*, 96, 5983-5986.

Sambur, J.B., Novet, T., Parkinson, B.A., 2010. Multiple Exciton Collection in a Sensitized Photovoltaic System. *Science*, 330, 63-66.

Santra, P.K., Nair, P.V., George Thomas, K., Kamat, P.V., 2013. CuInS₂-Sensitized Quantum Dot Solar Cell. Electrophoretic Deposition, Excited-State Dynamics, and Photovoltaic Performance. *J. Phys. Chem. Lett.*, 4, 722-729.

Shen, Q., Ayuzawa, Y., Katayama, K., Sawada, T., Toyoda, T., 2010a. Separation of ultrafast photoexcited electron and hole dynamics in CdSe quantum dots adsorbed onto nanostructured TiO₂ films. *Appl. Phys. Lett.*, 97, 263113-263113.

Shen, Q., Katayama, K., Sawada, T., Toyoda, T., 2008a. Characterization of electron transfer from CdSe quantum dots to nanostructured TiO₂ electrode using a near-field heterodyne transient grating technique. *Thin Solid Films*, 516, 5927-5930.

Shen, Q., Katayama, K., Sawada, T., Yamaguchi, M., Toyoda, T., 2006. Optical Absorption, Photoelectrochemical, and Ultrafast Carrier Dynamic Investigations of TiO₂ Electrodes Composed of Nanotubes and Nanowires Sensitized with CdSe Quantum Dots. *J. J. Appl. Phys.*, 45, 5569.

Shen, Q., Katayama, K., Yamaguchi, M., Sawada, T., Toyoda, T., 2005. Study of ultrafast carrier dynamics of nanostructured TiO₂ films with and without CdSe quantum dot deposition using lens-free heterodyne detection transient grating technique. *Thin Solid Films*, 486, 15-19.

Shen, Q., Kobayashi, J., Diguna, L.J., Toyoda, T., 2008b. Effect of ZnS coating on the photovoltaic properties of CdSe quantum dot-sensitized solar cells. *J. Appl. Phys.*, 103, 084304-084305.

Shen, Q., Toyoda, T., 2003. Studies of optical absorption and electron transport in nanocrystalline TiO₂ electrodes. *Thin Solid Films*, 438–439, 167-170.

Shen, Q., Yamada, A., Tamura, S., Toyoda, T., 2010b. CdSe quantum dot-sensitized solar cell employing TiO₂ nanotube working-electrode and Cu₂S counter-electrode. *Appl. Phys. Lett.*, 97, 123107-123103.

Sixto, G., Iván, M.-S., Lorena, M., Nestor, G., Teresa, L.-V., Roberto, G., Lina, J.D., Qing, S., Taro, T., Juan, B., 2009. Improving the performance of colloidal quantum-dot-sensitized solar cells. *Nanotechnology*, 20, 295204.

Toyoda, T., Oshikane, K., Li, D.M., Luo, Y.H., Meng, Q.B., Shen, Q., 2010. Photoacoustic and photoelectrochemical current spectra of combined CdS/CdSe quantum dots adsorbed on nanostructured TiO₂ electrodes, together with photovoltaic characteristics. *Journal of Applied Physics*, 108.

Yang, J., Oshima, T., Yindeesuk, W., Pan, Z., Zhong, X., Shen, Q., 2014. Influence of linker molecules on interfacial electron transfer and photovoltaic performance of quantum dot sensitized solar cells. *J. Mater. Chem. A*, 2, 20882-20888.

Yum, J.-H., Lee, J.-W., Kim, Y., Humphry-Baker, R., Park, N.-G., Grätzel, M., 2014. Panchromatic light harvesting by dye- and quantum dot-sensitized solar cells. *Sol. Energy*, 109, 183-188.

Zaban, A., Greenshtein, M., Bisquert, J., 2003. Determination of the Electron Lifetime in Nanocrystalline Dye Solar Cells by Open-Circuit Voltage Decay Measurements. *ChemPhysChem*, 4, 859-864.

Zhang, Y., Zhu, J., Yu, X., Wei, J., Hu, L., Dai, S., 2012. The optical and electrochemical properties of CdS/CdSe co-sensitized TiO₂ solar cells prepared by successive ionic layer adsorption and reaction processes. *Sol. Energy*, 86, 964-971.